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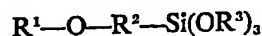
(54) DIRECT FILLING COMPOSITION FOR TEETH AND NOVEL FILLER FOR USE THEREIN

- (71) We, DENTAL FILLINGS LIMITED, a British Company, of 49 Grayling Road, London, N.16, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to compositions for the direct filling of teeth.
- It is known to use acrylic resins for filling teeth, and one successful type of such composition is described and claimed in our British Specification No. 721,641. However, it has been found that leakages may occur around the margins of fillings produced from acrylic resins within a relatively short time, and secondary caries may develop. It is believed that this marginal leakage is largely attributable to the fact that the coefficient of thermal expansion of the material is much greater than that of the tooth. This difference causes a "pumping" action to occur when the temperature in the mouth changes, and allows foreign material to penetrate between the filling and the tooth.
- Various attempts have been made to reduce the coefficient of thermal expansion of the filling material by incorporating in it a substance having a low coefficient of thermal expansion. Quartz and other forms of silica in a finely divided state have been proposed for this purpose. However, although such additives bring about a reduction in the coefficient of thermal expansion of the filler mass, the resulting mixtures exhibit other defects, principally reduction in mechanical strength of the set filling and difficulty in mixing the components under clinical conditions so as to form a homogeneous mixture.
- The present invention provides a new class of composition suitable for use in filling teeth, which is easy to handle, does not give rise to marginal leakage or development of secondary caries, does not discolour and has satisfactory aesthetic properties. In addition, the mechanical properties are improved when compared with non-reinforced acrylic acrylic resins or hitherto known acrylic resin systems to which fillers have been added.
- The present invention also provides a filler for use in dental filling compositions made by coating a silica or silicate filler of the kind described below with a vinyl silane primer, and then with an acrylic polymer. Fillers made in this way are readily wetted by the liquid resin during mixing of the filling composition and, in addition, become bonded to the resin when the resin has polymerised so as to bring about true reinforcement, that is an improvement in the general mechanical properties, of the filling.
- Fillers, which, when finely ground, are suitable for treatment and use in the present invention are of an inert nature, such as quartz (silica), fused siliceous materials, such as dental porcelain, and silicate glasses, particularly those having a negative coefficient of thermal expansion such as beta-eucryptite and the so-called pyrocerams. Another class of materials which are of particular utility are the complex compounds used as dental silicate cement powders.
- Dental silicate cements are well known and have been described in a number of publications, for example "The Science of Dental Materials" Skinner-Phillips, W. B. Saunders Co., 5th Edition 1960, Chapter 15, and "Restorative Dental Materials", ed. Peyton, C. V. Mosby Co., 2nd Edition 1964, page 506, *et sequ.* Dental silicate cements

are formed by the interaction of two components, a dental silicate cement powder and a dental silicate cement liquid. The former is produced by grinding a fused mass of complex composition, the nature of which is further described below, and the latter is usually a buffered solution of phosphoric acid. In our invention we utilise only the powder component.

While any type of currently available dental silicate cement powder can be used in the present invention, it is especially preferred to use a silicate cement powder made using a metal fluoride flux. The composition of such silicate cement powders (as described in the aforesaid "Restorative Dental Materials") is as follows, by weight: silica 32—42%; alumina 21—36%; trisodium or tricalcium phosphate 6—16%; and calcium fluoride, sodium fluoride or sodium aluminofluoride 13—35%. A typical composition contains by weight 38% silica, 30% alumina, 8% sodium or calcium phosphate, and 24% calcium or sodium fluoride. The use of dental silicate cement powders as fillers in the present invention is particularly advantageous for, in the presence of moisture, they provide a source of fluoride ions in minute concentration, and such ions have been shown to be beneficial in increasing the resistance of dental enamel to acids and thereby increasing the resistance of the tooth structure to caries. For use in the present invention, the filler must be in a finely divided form, and is, if necessary, ground to pass through a 200 British Standard mesh (which corresponds to a maximum particle size of about 75 microns).

According to our invention, the chosen filler of the kind hereinbefore specified is first coated with a vinyl silane primer, i.e. a silane having a sufficiently high content of aliphatic polymerizable $-\text{CH}=\text{C}<$ groups to be capable of copolymerisation with an acrylate or methacrylate monomer. The vinyl silane primers used in this invention are available commercially, and preferably conform to the general formula:



where R^1 is an acrylyl, methacryl, or crotonyl group, R^2 is an alkylene group of up to 4 carbon atoms, and R^3 is an alkyl group of up to 4 carbon atoms. *Gamma*-methacrylyloxypropyl-(trimethoxy) silane is available commercially under the trade names, Z 2030 of Dow Corning Corporation, and A 174 of Union Carbide Ltd., and is preferred.

The vinyl silane primer is applied to the chosen filler to give a silane coating of from 0.1 to 0.5 and preferably about 0.25 percent by weight of the uncoated filler. It is generally convenient first to prepare the primer in a volatile solvent, to apply the solution

to the filler, and to allow the solvent to evaporate.

The filler thus provided with a vinyl silane primer is then coated with an acrylic polymer. This is preferably carried out by applying to the primer-coated filler a liquid acrylic monomer containing a free radical polymerisation catalyst such as benzoyl peroxide and then heating the coated filler until polymerisation is complete. The preferred liquid acrylic monomer is methyl methacrylate, and the acrylic coating weight is in general from 0.5 to 20 percent, by weight of the filler carrying the vinyl silane coating only, a coating weight of about 2.5% being preferred. Alternatively, the vinyl silane primer-coated filler with applied monomer may be exposed in a suitable vessel to ultra violet light to bring about the desired polymerisation. Usually, after the polymer has been formed, it is necessary to grind the mass obtained, so that it will again pass through a 200 mesh screen. It is then ready for use as described below.

In an alternative procedure, the chosen filler, coated with the vinyl silane primer, is treated directly with a solution of polymethyl methacrylate or other solid acrylic resin in a suitable solvent, e.g. chloroform, and the solvent is then evaporated. Here also, grinding the mass obtained until it passes through a 200 mesh screen is generally necessary.

The treated fillers thus produced are added to dental filling compositions based on acrylic resin systems. Such compositions usually contain finely divided polymethyl methacrylate, or a copolymer of methyl methacrylate with a minor proportion of styrene, ethyl methacrylate, ethyl acrylate or other comonomer, and a monomer consisting mainly of methyl methacrylate to which is added 5 to 30% by weight of the mixture of monomers of acrylic or methacrylic acid (preferably the latter) and optionally up to 10% by weight of the monomer mixture of a modifying monomer such as ethyl methacrylate or other alkyl methacrylate, ethylene glycol dimethacrylate, or other vinyl monomer (i.e. monomer containing a $\text{CH}_2=\text{C}<$ group) to modify the hardness or other physical property of the polymer. Additionally, the composition may contain a catalyst system to bring about the polymerisation of the monomer. Suitable catalyst systems include tertiary amines in conjunction with organic peroxides (although the utility of these is limited because they cause the development of undesirable colour), mixtures of organic peroxides with sulphonic acid derivatives or especially thiol-based catalysts as described in our aforesaid Specification No. 721,641, i.e. a mixture of an organic peroxide, a copper compound, and a mercaptide accelerator selected from the zinc,

cadmium, lead, bismuth, alkaline earth metal and alkali metal salts or complexes formed with tertiary aliphatic mercaptans.

In practice, such compositions are normally supplied to the user in the form of two main components, one a powder and the other a liquid. The polymerisation catalyst system may be present in the powder or may be added separately, or, in the case of two component catalyst systems one component may be present in the powder and the other in the liquid. It is also possible to divide the powder into two parts and to add part of the catalyst to one part of the powder and the remainder of the catalyst to the other part, so producing a three component system. This can be especially useful where long shelf life is required. Immediately prior to use, the two (or three) components (powder and liquid) are mixed to form a thick cream or dough which is inserted into the prepared cavity in the tooth. Polymerisation of the monomeric constituent takes place under the influence of the catalyst and hardening of the mass occurs within a short time, ideally in about 3 to 5 minutes.

In the present invention, the organic polymer used in the powder component is replaced wholly or to a major extent by a filler treated as described above. The proportion of filler may vary according to the quantity of polymer deposited on the filler surface but should not be less than 50% by weight of the total powder component (not including any catalyst component therein). Minor proportions of other materials may be added to improve or modify the appearance of the final composition. Such material may include pigments to produce the colour shades required to match the colour of natural teeth and finely divided optical glasses having refractive indices of the same order as the resinous binder to improve the translucency of the final composition.

Preferred compositions in accordance with the present invention have the following composition (per 100 parts by weight of filler and polymethyl methacrylate):

	Parts by Weight
Filler in accordance with the present invention	50—90
Polymethyl methacrylate ...	50—10

These are mixed with a catalyst in accordance with our Specification No. 721,641, e.g. the following:

	Parts by Weight
Organic peroxide	2—4
Zinc tertiary dodecyl mercaptide	0.5—2
Copper methacrylate	0.01—0.06

All these ingredients are mixed together

and form the powder component. Alternatively, if longer shelf life (i.e. years rather than months) is required, the filler is divided into two parts, and one part is mixed with the polymer, peroxide, and copper salt, and the other part with the mercaptide. These ingredients are mixed at the time of use with a liquid which has the following composition (per 100 parts by weight):

	Parts by Weight
Methyl methacrylate	95—70
Methacrylate acid	5—30

In use, the powder is mixed with the liquid in the proportion of 3 to 4 parts by weight of powder to 1 part by weight of liquid. This gives a mix which is suitable for filling into teeth and has a setting time of 2 to 5 minutes.

The following Examples illustrate the manner in which the present invention may be practised.

EXAMPLE 1

A fused mass having an approximate composition of SiO_2 35%, $\text{Ca}_3(\text{PO}_4)_2$ 8%, Al_2O_3 23%, NaAlF_4 26%, and CaF_2 8% by weight was finely ground and passed through a 200 British Standard Mesh sieve. The ground material was divided into three parts and treated in the following manner:

- "A": Untreated ground material
- "B": Primed with gamma-methacryloxypropyl-(trimethoxy)-silane so as to give a primer coating of 0.2% by weight based on the untreated powder.
- "C": Primed as in "B" and then coated with polymethyl methacrylate. The coating was carried out by mixing the primed powder (100 parts by weight) with methyl methacrylate monomer (3.5 parts by weight) containing benzoyl peroxide (0.035 parts by weight), and heating at a temperature of 75—80°C. for a period of 12 hours. (This is the treatment of the invention).
- "D": A coating of polymethyl methacrylate was applied to the powder which had not been primed with the vinyl silane primer. The method of coating and the weight applied was the same as used in "C".

Each filler powder was then incorporated into a mixture having the following composition:

	Parts by Weight
Filler	80
Polymethyl methacrylate ...	16.62
Lauroyl peroxide	2.6
Zinc salt of tertiary dodecyl mercaptan	0.75
Copper methacrylate	0.03

3.8 parts by weight of the above mixture in each case was mixed with 1.0 part by weight of a mixture of methyl methacrylate monomer (80 parts by weight) and methacrylic acid (20 parts by weight). The mass hardened in approximately 5 minutes at ambient temperature (20—22°C.). Compression strength tests carried out on the resulting solids gave the following results:

10	Mix containing Filler "A" ...	11,940 p.s.i.
	Mix containing Filler "B" ...	17,050 p.s.i.
	Mix containing Filler "C" ...	21,100 p.s.i.
	Mix containing Filler "D" ...	14,360 p.s.i.

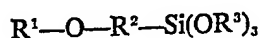
For comparative purposes a similar mix was made in which the filler was replaced by finely divided polymethyl methacrylate. 2 parts by weight of this mix were mixed with 1 part by weight of a mixture of methyl methacrylate monomer (80 parts by weight) and methacrylic acid (20 parts by weight) and allowed to harden at room temperature. Compressive strength tests carried out on the set mass gave a value of 12,370 p.s.i.

EXAMPLE 2

In a further experiment, finely ground high purity silica was primed with gamma-methacryloxypropyl - (trimethoxy) - silane and then coated with polymethyl methacrylate in the same manner as "C" in Example 1, and then incorporated into the same polymerizable composition. Compressive strength tests on the resulting hardened mass gave a value of 19,900 p.s.i.

WHAT WE CLAIM IS:—

1. A finely divided silica or silicate filler coated first with a vinyl-silane primer as hereinbefore defined and then with an acrylic polymer.
2. A filler according to claim 1 which is a coated dental silicate cement powder.
3. A filler according to claim 2 in which the said cement powder has the composition by weight: silica 32—42%; alumina 21—36% trisodium or tricalcium phosphate 6—16%; and calcium fluoride, sodium fluoride, or sodium aluminofluoride 13—35%.
4. A filler according to any of claims 1 to 3 having a maximum particle size of about 75 microns.
5. A filler according to any of claims 1 to 4 in which the vinyl silane coating is present in an amount of 0.1 to 0.5% by weight of the uncoated filler.
6. A filler according to any of claims 1 to 5 in which the vinyl silane is of the formula:



where R^1 is an acrylyl, methacrylyl, or crotonyl group, R^2 is an alkylene group of up to 4 carbon atoms, and R^3 is an alkyl group of up to 4 carbon atoms.

7. A filler according to claim 6 in which the vinyl silane is gamma-methacryloxypropyl-(trimethoxy)silane.

8. A filler according to any of claims 1 to 7 in which the acrylic polymer coating is present in an amount of 0.5 to 20% by weight of the filler carrying the vinyl silane coating only.

9. A filler according to any of claims 1 to 8 in which the acrylic polymer is polymethyl methacrylate.

10. A filler according to claim 1 substantially as hereinbefore described.

11. A composition for filling dental cavities comprising (A) a filler as claimed in any of claims 1 to 10, (B) up to an equal weight of polymethyl methacrylate or of a copolymer of methyl methacrylate with a minor proportion of a comonomer, (C) a monomer mixture comprising methyl methacrylate, 5 to 30% by weight of the mixture of methacrylic or acrylic acid, and optionally up to 10% by weight of the mixture of another comonomer, and (D) a catalyst to promote polymerisation of the monomers (C).

12. A composition according to claim 11 in which the catalyst (D) is a mixture of an organic peroxide, a copper compound, and a mercaptide accelerator selected from the zinc, cadmium, lead, bismuth, alkaline earth metal and alkali metal salts or complexes formed with tertiary aliphatic mercaptans.

13. A composition according to claim 12 in which the catalyst (D) is a mixture of an organic peroxide, zinc tertiary dodecyl mercaptide, and copper methacrylate.

14. A composition according to claim 13 comprising (I) per 100 parts by weight of filler and polymethyl methacrylate, 50—90 parts by weight of the filler, 50—10 parts by weight of polymethyl methacrylate, 2—4 parts by weight of an organic peroxide, 0.5 to 2 parts by weight of zinc tertiary dodecyl mercaptide, and 0.01 to 0.06 part by weight of copper methacrylate, and (II) per 100 parts by weight, 95—70 parts by weight of methyl methacrylate and 5—30 parts by weight of methacrylic acid, in the proportion of 3 to 4 parts by weight of (I) to 1 part by weight of (II).

15. A composition according to claim 11 substantially as hereinbefore described.

16. A two-component pack for producing compositions for filling dental cavities comprising, in a first pack (I), (A) a filler as claimed in any of claims 1 to 10, (B) up to an equal weight of polymethyl methacrylate or of a copolymer of methyl methacrylate with a minor proportion of a comonomer, and (D) a catalyst to promote

- polymerisation of methyl methacrylate, and in a second pack (II), (C) a mixture comprising methyl methacrylate, 5 to 30% by weight of the mixture of methacrylic or acrylic acid and optionally up to 10% by weight of the mixture of another comonomer.
17. A two-component pack according to claim 16 comprising, in a first pack (I) per 100 parts by weight of filler and polymethyl methacrylate 50—90 parts by weight of the filler 50—10 parts by weight of polymethyl methacrylate, 2—4 parts by weight of an organic peroxide, 0.5 to 2 parts by weight of zinc tertiary dodecyl mercaptide, and 0.01 to 0.66 part by weight of copper methacrylate, and in a second pack (II), per 100 parts by weight, 95 to 70 parts by weight of methyl methacrylate and 5—30 parts by weight of methacrylic acid.
18. A three-component pack for producing compositions for filling dental cavities comprising, in a first pack (Ia) a filler as claimed in any of claims 1 to 10, 50—10 parts by weight of polymethyl methacrylate, 2—4 parts by weight of an organic peroxide, and 0.01 to 0.06 part by weight of copper methacrylate, in a second pack (Ib) additional filler as claimed in any of claims 1 to 10 up to a total of 50—90 parts by weight in packs (Ia) and (Ib), and 0.5 to 2 parts by weight of zinc tertiary dodecyl mercaptide, the said parts in packs (Ia) and (Ib) being per 100 parts by weight of filler and polymethyl methacrylate in combined packs (Ia) and (Ib) and in a third pack (II) per 100 parts by weight, 95—70 parts by weight of methyl methacrylate, and 5—30 parts by weight of methacrylic acid.

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